

FINAL REPORT

NAG3-1846 – STRUCTURE, HYDRODYNAMICS, AND PHASE TRANSITION OF FREELY SUSPENDED LIQUID CRYSTALS

PERIOD:

May 2, 1996 – May 1, 2000

PRINCIPAL INVESTIGATOR:

Noel A. Clark
Professor of Physics
Department of Physics
University of Colorado
Boulder, CO 80309-0390
Phone: (303) 492-6420
Fax: (303) 492-2998
noel.clark@colorado.edu

DATE:

September 25, 2000

SUMMARY OF RESEARCH

1. - Background and Research Themes

Smectic liquid crystals are phases of rod shaped molecules organized into one dimensionally (1D) periodic arrays of layers, each layer being between one and two molecular lengths thick. In the least ordered smectic phases, the smectics A and C, each layer is a two dimensional (2D) liquid. Additionally there are a variety of more ordered smectic phases having hexatic short range translational order or 2D crystalline quasi long range translational order within the layers [1]. The inherent fluid-layer structure and low vapor pressure of smectic liquid crystals enable the long term stabilization of freely suspended, single component, layered fluid films as thin as 30Å, a single molecular layer [2,3,4]. The layering forces the films to be an integral number of smectic layers thick, quantizing their thickness in layer units and forcing a film of a particular number of layers to be physically homogeneous with respect to its layer structure over its entire area. Optical reflectivity enables the precise determination of the number of layers [4].

These ultrathin freely suspended liquid crystal films are structures of fundamental interest in condensed matter and fluid physics. They are the thinnest known stable condensed phase fluid structures and have the largest surface-to-volume ratio of any stable fluid preparation, making them ideal for the study of the effects of reduced dimensionality on phase behavior and on fluctuation and interface phenomena. Their low vapor pressure and quantized thickness enable the effective use of microgravity to extend the study of basic capillary phenomena to ultrathin fluid films.

Freely suspended films have been a wellspring of new liquid crystal physics. They have been used to provide unique experimental conditions for the study of condensed phase transitions in two dimensions. They are the only system in which the hexatic has been unambiguously identified as a phase of matter [1], and the only physical system in which fluctuations of a 2D XY system and Kosterlitz Thouless phase transition has been observed [4] and 2D XY quasi long range order verified [5]. Smectic films have enabled the precise determination of smectic layer electron density and positional fluctuation profile [6] and have been used to show that the interlayer interactions in antiferroelectric tilted smectics do not extend significantly beyond nearest neighbors [7].

The interactions which are operative in liquid crystals are generally weak in comparison to those in crystalline phases, leading to the facile manipulation of the order in liquid crystals by external agents such as ap-

plied fields and surfaces. Effects arising from weak ordering are significantly enhanced in ultrathin free films and filaments wherein the intermolecular coupling is effectively reduced by loss of neighbors.

Over the past four years this research, which we now detail, has produced a host of exciting new discoveries and unexpected results, maintaining the position of the study of freely suspended liquid crystal structures as one of most exciting and fruitful areas of complex fluid physics. In addition, several potentially interesting microgravity free film experiments have been identified.

2. - Work Carried Out under NASA Grant NAG3-1846

In this Section we detail the work carried out over the past four years under this Grant. Publications resulting from the support of NASA Grant NAG3-1846 are listed in Section 3 and indicated by a **Publication Number [P#]** when cited. Results are reported in the following project areas, which were outlined in the NAG3-1846 proposal:

- Generation and exploration of freely suspended liquid crystal bubbles.
- Exploration of the role of curvature in determination of film structure.
- Study of the in-plane layer structure of freely suspended liquid crystal films.
- Molecular dynamics computer simulation of smectic film layer structure.

2.1 - HIGHLIGHTS OF WORK CARRIED OUT UNDER NASA GRANT NAG3-1846

Bent core (banana-shaped) molecules: Pasteur's experiment in a fluid

- discovery of the spontaneous formation of macroscopic domains of a chiral phase in a fluid smectic of achiral banana-shaped molecules.
- observation of chiral domains in two- and three-layer films of achiral banana-shaped molecules.
- demonstration that the chiral phase ground state is antiferroelectric.

Generation and manipulation of smectic liquid crystal bubbles

- development of techniques for inflating and holding smectic liquid crystal bubbles.
- measurement of the gas permeability of few layer thick liquid crystal films.
- generation of dense island arrays on few layer thick films.

Bent core (banana-shaped) molecules: Discovery of freely suspended smectic filaments

- nested cylinder layer geometry.
- observation of a compression-induced buckling instability to a helical structure.

Study of (+1, -1) topological pair annihilation and defect-island interaction

- the simplest liquid crystal defect dynamical process.
- apparent defect mobility decreases with separation, whereas theory predicts an increase.
- analysis of thermal fluctuation effects.

Determination of in-plane polarization in tilted smectic films

- first unambiguous evidence for single layer alternation of polarization direction in antiferroelectric smectics.
- first observation of fracture of the orientation field in a liquid crystal via coupling of surface polarization to in-plane electric field.
- observation of ferroelectric ordering of the surface polarization of the tilted surface layers of an un-tilted (smectic A) film.

Study of tilted smectic films in a rotating in-plane electric field

- winding of orientational solitons.
- theoretical modeling of soliton velocity.
- modulation of soliton width by orientational elastic anisotropy.
- relaxation of ring patterns to determine orientational diffusion coefficient.

Atomistic molecular dynamics simulation of smectic structure

- development of a state-of-the-art force field for liquid crystal simulation.
- simulation of the layer structure of untilted (smectic A) and tilted (smectic C) phases.
- study of nanosegregation in smectic layered solvents, including discovery of photo-induced nano-phase segregation.

2.2 - DETAILS OF WORK CARRIED OUT UNDER NASA GRANT NAG3-1846

Bent core (banana-shaped) molecules: Pasteur's experiment in a fluid [P12,P9]

We have made a major discovery in condensed matter science, finding macroscopic chiral domains in a fluid phase of achiral molecules. Our observation follows a line of study of the relationship between macroscopic and molecular chirality that was begun by Pasteur in 1848. He found that crystals of a molecularly chiral salt of "racemic acid" existed in left and right handed forms - the left and right handed molecules spontaneously segregating into macroscopically left and right-handed chiral crystals respectively. Subsequently there have been many observations of coexisting domains of opposite handedness crystallized from molecules which are chiral as well as achiral in isotropic solution (achiral molecules). In the latter cases the molecules adopt chiral conformations which pack more effectively than achiral conformations. However, in the 150 years since Pasteur, all observations of such spontaneous chiral segregation have been made in crystal phases. Ours is the first such observation in a fluid. These results appeared in *Science* in December, 1997 and were the subject of a *Science* "Research News" article, shown at the right, in March, 1998. The molecules which form the SmCP_A, first synthesized in Japan in 1994 by Matsunaga, are "bow" or "banana"-shaped as a result of their bent core. Their highest temperature smectic phase was first identified as a SmC, but then, by the Tokyo Tech (Takezoe) group in 1996, as SmA with the possibility of polar ordering. Using samples of the Matsunaga and Takezoe compounds, we were able to show that the phase was indeed tilted (SmC). Moreover, our experiments, in particular those on freely suspended films, revealed an amazing feature of this phase missed in the earlier work: the spontaneous breaking of achiral symmetry. This achiral symmetry breaking results from the combined effect of the two distinct intralayer broken symmetries shown in **Figure 1**: polar ordering of the molecular bows (with their arrows pointing in a particular direction, clearly a consequence of the bent shape), and molecular tilt (rotation about the arrows). This discovery indicates that a rich variety of novel structures and phases will be available from these more complex molecular shapes.

Generation and manipulation of smectic liquid crystal bubbles

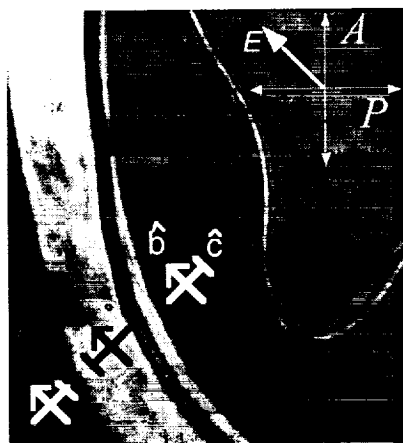
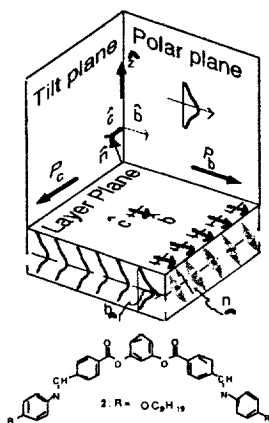


Figure 1: (left) Layer structure of the chiral phase formed from bent-core molecules, showing the achiral bent-core molecule, the polar ordering of the molecular bows along **b** and the tilt in the direction **c**, which combine to make the layer chiral. (right) Depolarized reflected light micrograph of a three layer thick chiral freely suspended film formed from bent-core molecules, showing the bright and dark domains of opposite handedness, aligned by the in-plane field **E** to have uniform polar direction **b**, but with opposite tilt directions **c**. The multilines are 2π reorientations trapped by the field. From [P12].

The inherent fluid-layer structure and low vapor pressure of smectic liquid crystals enable the long term stabilization of freely suspended, single component, layered fluid films as thin as 30Å, a single molecular layer. Stable spherical films of low vapor pressure fluid are potentially quite interesting and useful for a variety of studies of the flow and fluctuation properties of thin fluid films. The formation and manipulation of smectic bubbles has thus been a focus of our work. Our initial studies were complicated by a geometry requiring very slow filling during the critical period when the bubble reaches its minimum radius of curvature as a hemispherical cap at the end of the hypodermic needle. Analysis of this problem indicated that we needed to minimize the gas volume behind the bubble and with this change we were able to generate smec-

no liter-
crystal, in-

LIQUID CRYSTALS

Chiral Order from Achiral Molecules

Gerd Heppke and Dirk Moro

Chirality, the handedness of matter, and ferroelectricity, resulting from macroscopic electric polarization, are properties that had been believed to exist independently from each other. However, liquid crystals show a remarkable interplay between these phenomena, a fact that has great technological significance for display devices. Up to now, these ferroelectric displays use liquid crystals, which need to possess a chiral molecular structure. But in 1996, Niori et al. reported that a similar ferroelectric switching was observed in a liquid-crystalline phase formed by achiral molecules with a bow-shape resembling the form of a banana (1). Even though the molecules are achiral, these materials are able to form macroscopic chiral domains and, as Link et al. reported in a recent paper in *Science*, exhibit a spontaneous breaking of achiral symmetry in a bulk liquid crystal (2).

Max Born introduced the idea of creating a polar fluid as early as 1916 (3) in order to explain the formation of a nematic phase by dipolar interaction between the perma-

nent dipoles of rodlike molecules. Although the proposed mean-field model was able to predict a transition from an isotropic phase to an anisotropic one, it had two major deficiencies. First, the dipolar interaction of the permanent dipoles of molecules forming nematic phases is too weak to produce a phase transition at room temperature, where it occurs. Worse, nematic phases are also formed by molecules that do not possess a permanent dipole at all. Second, the resulting anisotropic order of dipoles is such that, on average, the dipoles point in the same direction, so that an inherently ferroelectric fluid was predicted, but such a polar order was never found experimentally in nematic liquid-crystalline phases. Actually, the rod-shaped molecules exhibit a preferred parallel orientation, and even when the molecules bear a permanent dipole, there are, on average, as many dipoles pointing "up" as there are dipoles pointing "down."

According to this picture of the nematic phase, it was accepted for a long time that macroscopic polar order could not exist in liquid crystalline phases in general. However, this view had to be revised when Meyer et al. (4) showed by a simple symmetry argument that layered liquid crystalline

SCIENCE • VOL. 279 • 10 MARCH 1998 • www.sciencemag.org

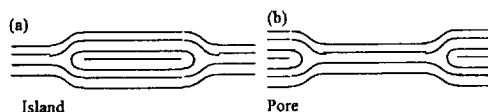


Figure 2: Schematic film profiles for islands and pores. The change in layer number is achieved by dislocations.

by filling the bubble with a permeant gas, such as helium, and monitoring the time rate of change of bubble radius. The gas permeability of films which are only a few molecular layers thick and its dependence on film thickness have never been measured but are fundamental properties. The helium permeability of liquid crystal bubbles was measured by filling them with helium and observing the decrease of radius as the helium diffuses out through the film. This permeation is fairly spectacular: a two layer thick, 2 centimeter diameter bubble filled with 1 atm helium and surrounded by air will deflate by the leakage of helium through the film in about 10 seconds. The radius vs. time data was employed to determine helium permeability, which is about 1000 He atoms/sec/LC molecule for a two layer film. One of the techniques was to detach bubbles from the needle and levitate them. However, gas rapidly leaks via permeation out of few layer thick bubbles, reducing their radius with time. Thus experiments were carried out with the bubbles still attached to the needle.

A second class of experiments performed focused on the behavior of island arrays on bubbles. Islands are pancake-like stacks of extra layers on an otherwise uniform thickness film, as shown in Figure 3. Islands are of interest as statistical mechanical and dynamical objects because of their very small mass (10^{-12} gm for a $10\text{ }\mu\text{m}$ diameter island), and coupling to the 2 dimensional fluid film. Swirling the bubble with an air jet generates a two-dimensional foam of islands which is quite stable against island aggregation, which takes place very slowly. The islands respond in a polar way to applied electric field, indicating that they are either charged or significantly more polarizable than the surrounding film. In a microgravity environment the Perrin length, $k_B T/mg$ for an island will be large compared to the bubble size, meaning that in this case the islands will be thermally dispersed over the bubble surface. Interactions between islands can be controlled by charging the sphere.

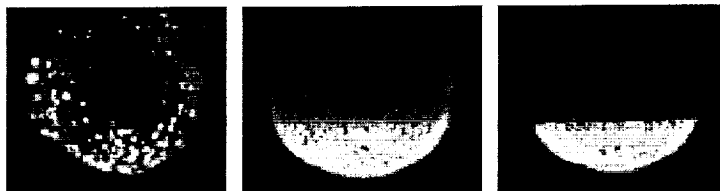


Figure 3: Islands sedimenting on a freely suspended 8CB smectic bubble. **Figure 11:** Photographs showing smectic C bubbles, $\sim 20\text{ mm}$ in diameter, viewed in reflected light. The dark parts of the bubbles are ~ 3 to 5 smectic layers thick. The pancake shaped islands (Figure 2) having additional layers are evident. The black spot in the center of the bubbles is an illumination artifact. In the bubble geometry the ratio of the plateau border length around the needle to the film area is very small relative to planar films. This enables the formation of island arrays by a slight decrease of internal pressure. Islands can be dispersed on the film by an air jet (left), but in 1 g sediment to the bottom of the bubble within a few minutes (right).

Bent core (banana-shaped) molecules: Discovery of freely suspended smectic filaments [P9]

We have for many years endeavored to make filaments of smectic liquid crystals having the nested cylindrical layer structure shown in Figure 4, a geometry that would enable a variety of experiments on smectics that have highly curved, defect-free layers. These efforts failed until recent experiments



Figure 4: Freely suspended filaments in a transverse electric field. Filaments are observed in reflected light with crossed polarizers, the optic axis being parallel to the axis of the filaments. In some filaments (in this case the top filament) a π reorientation of the optic axis is trapped as is indicated by the arrow in the microphotographs. This reorientation moves at a constant velocity along the length of the filament when an electric field is applied normal to the filament, moving from one end of the filament to the other with one sign of field and vice-versa. The diameter of the filament is $13\text{ }\mu\text{m}$ while its length is over 2 mm .

done with films of a chiral homolog [P9] of the bent-core molecule in **Figure 1**. Attempts to make films by the usual spreading technique yielded freely suspended filaments up to several millimeters long and 2-20 μm in diameter. These filaments were locally uniform in width, with the width changing via discrete jumps. Some filaments were lath-shaped and could be wound into a helix by pulling the filament between a pin and cup and rotating the pin. The filament responded to an electric field applied normal to its axis. Such filaments offer exciting possibilities for study of the spontaneously chiral phases formed by bent-core molecules. They are highly ordered single domain preparations, making them ideal for high resolution x-ray study of the chiral phase structure.

Study of (+1, -1) topological defect pair annihilation in 2 and 3 layer films

We have studied the attraction and annihilation of pairs of opposite strength topological defects in two layer thick freely suspended smectic C films. These are generated in quenches (from the smectic C to the smectic A and back), by collapse of a free film bubble from spherical to planar shape, which generates many defects. The defects annihilate in pairs until there are only two left. These last two are observed via reflected light microscopy. **Figure 5a** shows a typical pair of annihilating defects. For each such event, the separation, r , vs. time is measured and data for a series of events is used to find the average collapse rate dr/dt as a function of r . These data are shown in **Figure 5b**. The results are surprising. Current theoretical models of the annihilation process assume that the defects undergo diffusive Brownian motion while attracting via a two dimensional coulomb ($1/r$) force. This predicts that at a given separation the rate of approach, dr/dt ,

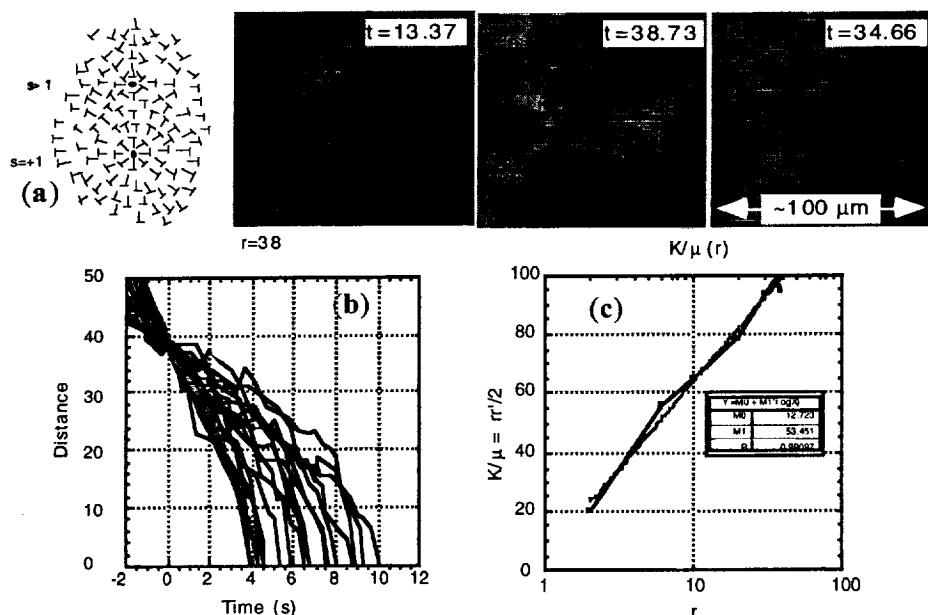


Figure 5: (a) Annihilating +1 and -1 topological defects imaged by depolarized reflected light video microscopy. (b) Plot of $r(t)$, defect separation vs. time, from the video records, with $t = 0$ corresponding to a defect separation of 38 μm . The solid gray curve is $dr/dt \sim K/\eta(1/r)$, the deterministic prediction given K/η measured from dr/dt at $t = 0$. However, the approach for $t > 0$ is slower than this prediction for nearly all observed trajectories. Similar behavior is observed for all other starting separations. (c) The effective K/η decreases with separation r as $\log(r)$, showing that the rate of approach of annihilating defects becomes progressively slower than deterministic as their separation decreases.

should behave as $1/r$ and $r(dr/dt) = \text{constant}$. However our experiments show a clearly different behavior, with $dr/dt \sim (1/r)\log(r)$. This observation indicates that the current theoretical understanding of the fluctuation behavior of topological defects is flawed, a problem of fundamental interest with wide ranging implications in statistical physics (for example, in describing the physics of vortex motion in superconductors and the kinetics of the early universe).

Determination of in-plane polarization in tilted smectic films [P1,P4,P5,P6,P9,P12,P15]

We have obtained a very beautiful result in freely suspended films of the antiferroelectric liquid crystal material MHPOBC, obtaining the first unambiguous evidence for longitudinal ferroelectricity in a liquid crystal and, at the same time, developing a technique for distinguishing ferroelectric from antiferroelectric ground states in tilted smectic phases. **Figure 6** sketches the experiment, showing a

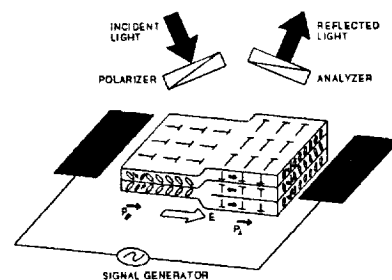


Figure 6: DRLM observation of in-plane film polarization. Even layer number films have longitudinal polarization (in the tilt plane), whereas odd layer number films have transverse polarization (normal to the tilt plane). From [P15].

portion of a freely suspended film, incident and reflected light to probe the orientation of the molecular tilt direction in the film plane, electrodes for applying an electric field in the film plane, and sections of the film where it is two and three layers thick. Where the film has an even number of layers the surface induced polarizations give a net polarization in the direction of the molecular tilt, and the single layer transverse polarizations due to chirality cancel. As a result, in an applied electric field the tilt direction aligns parallel to the field. However, where the film is an odd number of layers thick the surface polarizations do not, adding to give the net polarization of a single layer. **Figure 6** shows the molecules and the longitudinal and transverse polarizations in the two cases. **Figure 7** shows the orientation of the resulting polarization and tilt direction in an applied field, with the tilt direction, indicated by a "T", normal to the polarization, indicated by an "→", for an odd number of layers, and parallel to the polarization for an even number of layers. With appropriate optics the two tilt orientations can be visualized as black and bright in reflected light (**Figure 7a**). The image in **Figure 7b** shows a reflected light micrograph of such a film in an applied field. This discovery will enable the first measurement of longitudinal polarization and a detailed comparison of longitudinal and transverse liquid crystal polarizations.

We have used this technique in a variety of ways, establishing that the ground state of the bent core phases is antiferroelectric [P9,P12], and showing that the so called "thresholdless antiferroelectric" tilted smectic phase is actually a ferroelectric smectic C [P4,P5].

This work has also been extended to exploit electric field coupling to ferroelectric surface ordering in achiral freely suspended films [P1,P6]. In a smectic C film the molecules are tilted, yielding ferroelectric order at the surface. The uniform tilt through the film yields *opposite polarization on the two surfaces*. With the application of an electric field these polarizations flip to be along the field, some regions going clockwise and others counterclockwise. Such opposite rotation produces line defects where the polarization rotates rapidly through π radians (π -walls). The π -walls form an interesting pattern on the surface of the film. There are two sets of weakly interacting walls, one set on each surface, shown in **Figure 8**. This interesting observation will enable

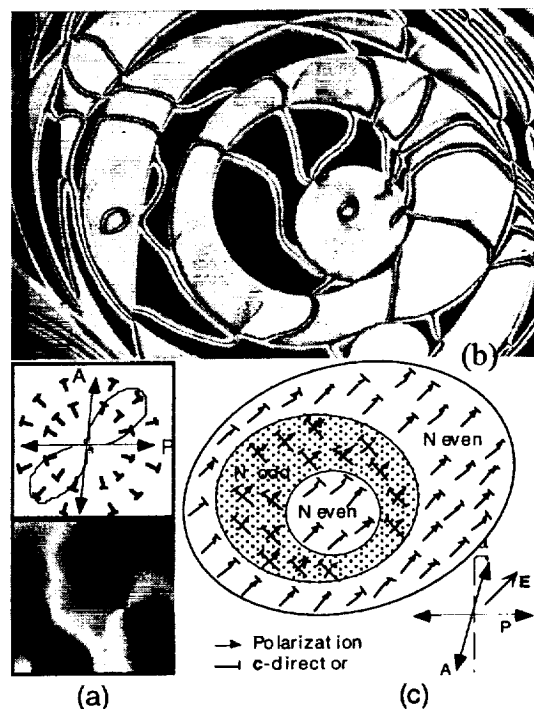


Figure 7: (a) DRLM polarizer and analyzer orientation enabling distinction of director orientations 90° apart. (b) DRLM photomicrograph showing longitudinal polarization in even layer number regions and transverse polarization in odd layer number regions. (c) Schematic of the tilt direction and polarization in (b). From [P15].

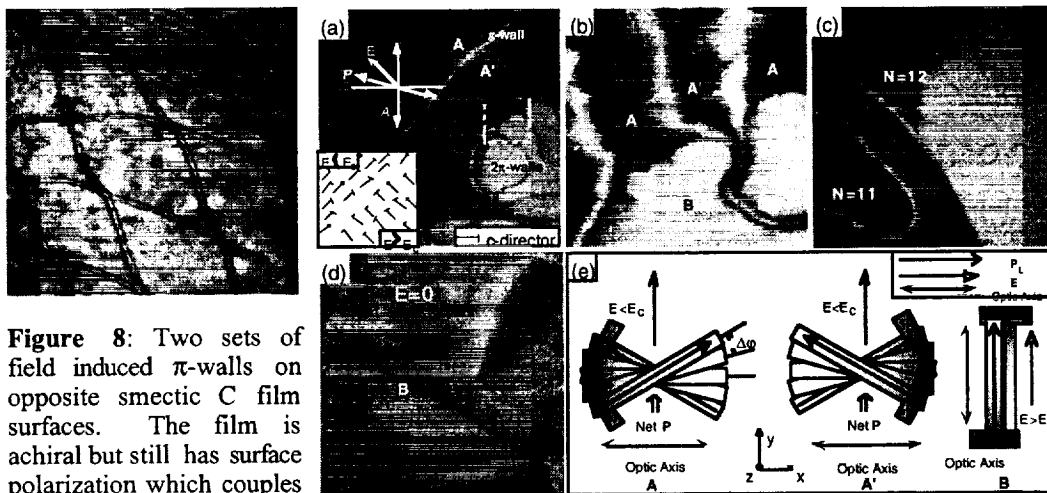


Figure 8: Two sets of field induced π -walls on opposite smectic C film surfaces. The film is achiral but still has surface polarization which couples to the field.

Figure 9: (a-d) DRLM photos showing orientation fracture [white areas in (a-c)] induced by electric field coupling to the surface polarization. (d) Metastable fracture domain persisting after field removal, indicative of a metastable anticlinic interface in this (synclitic) smectic C phase. (e) schematic of the orientational fracture. From [P1].

us to measure the surface polarization and elastic coefficients. This line of research has yielded two novel liquid crystal phenomena. By applying a sufficiently large electric field we can apply a torque to the orientation field that is sufficiently large to fracture it [P1], yielding, in a smectic C film [where the molecule tilts are synclinic (in the same direction) in adjacent layers], a single interface where the molecules tilt in opposite directions, as illustrated in **Figure 9**. This interface is metastable, persisting for several minutes once the field is removed, showing that there is a metastable minimum at the anticlinic orientation in the interlayer orientational potential energy.

Additionally, we have found that the tilt orientations on the film surface become anticlinic at high temperatures where the film interior is smectic A (molecules not tilted) [P6]. Thus, the tilted surface layers on the two sides of an untilted film interact to favor opposite orientation. A variety of possible explanations for this effect have been considered, including van der Waals interactions and fluctuation confinement, but at present it is a complete mystery.

Study of tilted smectic films in a rotating in-plane electric field [P2]

The combination of fluidity and local anisotropy which characterizes ferroelectric smectic C* films is effectively probed by application of an in-plane electric field. Particularly interesting is the response when the field rotates in the film plane. In this case the tilt direction reorients along with the field in the film center but is pinned with fixed orientation at the film edge, necessitating the formation of an orientational soliton with each 2π rotation of the field. The solitons reflect the film shape, forming rings on a circular film. The characteristic spacing of the soliton depends on the applied field strength, as shown in **Figure 10**. The solitons move toward the film center with a velocity that increases with applied field strength.

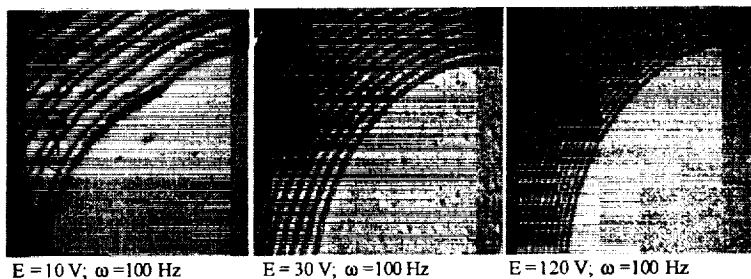


Figure 10: Soliton rings formed by a rotating electric field. As the field rotates each soliton moves toward the film center with a velocity that varies with E as $1/E^2$. From [P2].

With the field removed the ring patterns provide a useful probe of the liquid crystal elastic anisotropy, the rings being wider in regions where the deformation having the larger elastic constant is dominant (**Figure 11**). The orientational diffusion constant can be measured by observation of the relaxation of the ring pattern once the field is set to zero. See **Figure 12**.

Figure 11: A fully developed ring pattern with the field removed involves both splay and bend of the orientation field. The splay elastic constant is larger, making the rings wider in the splay regions. In films with large polarization this situation is reversed, with the bend regions being broader. From [P2].

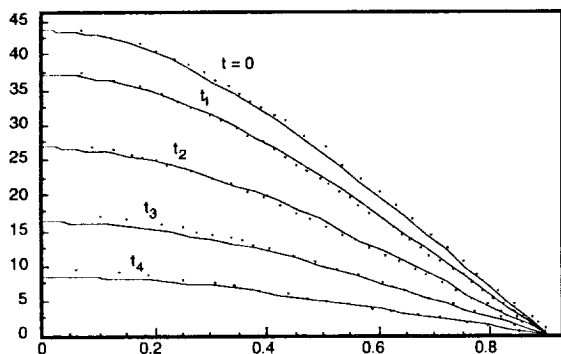
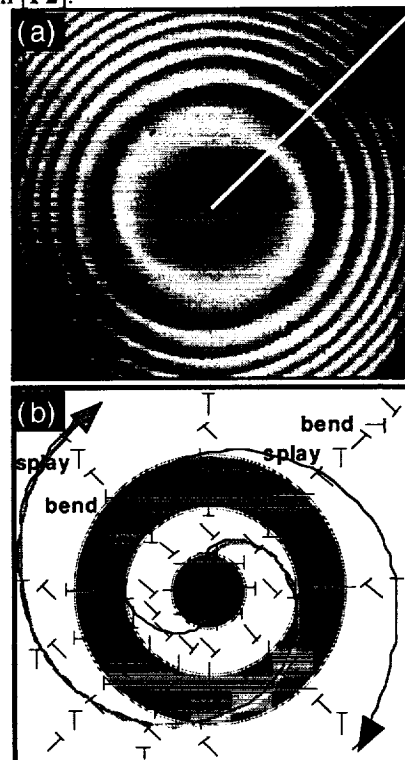


Figure 12: Net director winding in units of 2π turns vs fractional radial position on the film in units of the film radius for various times showing relaxation of the ring pattern when field is removed. The solid curves are fits to the orientational diffusion equation. From [P2].

The computational component of this research focuses on improving our understanding of liquid crystal nanophysics via direct atomistic simulation of molecular organization in smectics, in particular the layering in smectics and the behavior of solutes in smectic films. During the past several years we have developed a variety of effective computational tools for the simulation of molecularly realistic liquid crystal models, and have begun to apply them to understanding smectic structure [P8]. These tools include a hybrid *ab initio*/empirical force field specifically designed for modeling liquid crystalline materials and special simulation techniques (multiple-timestep molecular dynamics, hybrid Monte Carlo, particle-mesh Ewald method) enabling efficient configuration-space and conformational sampling. A highly accurate force field is required because the self-organization of soft materials such as LCs is governed by the interplay of a variety of subtle energetic and entropic effects, which must be adequately quantified.

These methods have been applied to the study of solute distribution in a smectic phase, under conditions where the shape of the solute molecules, in this case the azo dye 7AB, can be changed from linear (*trans*) to bent (*cis*) optically. We find a distinctive photo-induced nanosegregation, the 7AB intercalating between and expanding the layers upon *trans* to *cis* isomerization. Quantitative agreement with measured layer expansion indicates that the simulation accuracy is adequate for a variety of films-related problems.

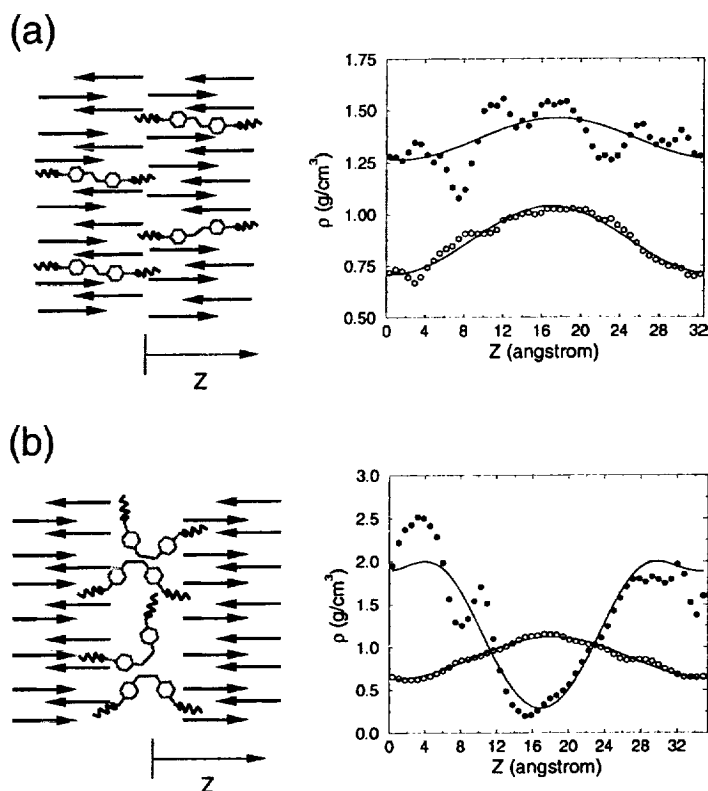


Figure 12: (left) Schematic of the nanometer scale organization of the azo dye 7AB in a smectic solvent. (right) Mass density profiles along the layer normal for 8CB (open circles) for a *trans*-7AB/8CB mixture (a) and for a *cis* 7AB/8CB mixture (b). In the *trans* state the 7AB locates preferentially in the smectic layers, whereas in the *cis* state it nanosegregates between the layers. The calculated layer expansion which results matches that found in experiments. From [P7].

3. - Publications and Presentations Resulting from Research Supported by NASA Grant NAG3-1846

Publications

- [P1] "ORIENTATIONAL FIELD FRACTURE IN A LIQUID CRYSTAL: METASTABLE ANTICLINIC MOLECULAR TILT IN ADJACENT LAYERS IN A SMECTIC C," D.R. Link, G. Natale, J.E. MacLennan, N.A. Clark, M. Walsh, S.S. Keast, and M.E. Neubert, *Physical Review Letters* **83**, 3665-3668 (1999).
- [P2] "RING PATTERN DYNAMICS IN SMECTIC-C* AND SMECTIC- C_A* IN FREELY SUSPENDED FERROELECTRIC LIQUID CRYSTAL FILMS," D.R. Link, J.E. MacLennan, L. Radzihovsky, and N.A. Clark, *Physical Review Letters* **84**, 5772-5775 (2000).
- [P3] "HFF: A FORCE FIELD FOR LIQUID CRYSTAL MOLECULES," E. Garcia, M.A. Glaser, N.A. Clark, and D.M. Walba, *Journal of Molecular Structure (Theochem)* **464**, 39-48 (1999).
- [P4] "THE CASE OF THRESHOLDLESS ANTIFERROELECTRICITY: POLARIZATION-STABILIZED TWISTED SMC* LIQUID CRYSTALS GIVE V-SHAPED ELECTRO-OPTIC RESPONSE," N.A. Clark, J.E. MacLennan, R. Shao, D.A. Coleman, S. Bardon, T. Bellini, D.R. Link, G. Natale, M.A. Glaser, D.M. Walba, M.D. Wand, X.-H. Chen, P. Rudquist, J.P.F. Lagerwall, M. Buivydas, F. Gouda, and S.T. Lagerwall, *Journal of Materials Chemistry* **9**, 1257-1261 (1999).
- [P5] "UNRAVELING THE MYSTERY OF THRESHOLDLESS ANTIFERROELECTRICITY: HIGH CONTRAST ANALOG ELECTRO-OPTIC EFFECTS IN CHIRAL SMECTICS C," P. Rudquist, R. Shao, D.A. Coleman, S. Bardon, D.R. Link, T. Bellini, J.E. MacLennan, X.-H. Chen, D.M. Walba, J.P.F. Lagerwall, M. Buivydas, F. Gouda, S.T. Lagerwall, and N.A. Clark, submitted to *Physical Review Letters*.
- [P6] "ANTICLINIC SMECTIC-C SURFACES ON SMECTIC-A FREELY SUSPENDED LIQUID-CRYSTAL FILMS," D.R. Link, G. Natale, N.A. Clark, J.E. MacLennan, M. Walsh, S.S. Keast, and M.E. Neubert, *Physical Review Letters* **82**, 2508-2511 (1999).
- [P7] "PHOTOCONTROLLED NANOPHASE SEGREGATION IN A LIQUID CRYSTAL SOLVENT," Y. Lansac, M.A. Glaser, N.A. Clark, and O.D. Lavrentovich, *Nature* **398**, 54-57 (1999).
- [P8] "ATOMISTIC SIMULATION AND MODELING OF SMECTIC LIQUID CRYSTALS" M.A. Glaser, in *Advances in the Computer Simulation of Liquid Crystals*, C. Zannoni and P. Pasini, ed (Kluwer, Dordrecht, 1999).
- [P9] "THE SMECTIC XP PHASES: CHIRAL LIQUID CRYSTALS FROM ACHIRAL MOLECULES," D.M. Walba, E. Korblova, R.F. Shao, J.E. MacLennan, D.R. Link, and N.A. Clark, Proceedings of the Fifth International Display Workshops of the Society for Information Display, Kobe, Japan (1998).
- [P10] "TOPOLOGICAL INCLUSIONS IN 2D SMECTIC C FILMS," D. Petkey, T.C. Lubensky, and D.R. Link, *Liquid Crystals* **25**, 579-587 (1998).
- [P11] "SURFACE TENSION OBTAINED FROM VARIOUS SMECTIC FREE-STANDING FILMS: THE MOLECULAR ORIGIN OF SURFACE TENSION," P. Mach, C.C. Huang, E.D. Wedell, T. Nguyen, W.H. deJeu, F. Guittard, J. Naciri, R. Shashidhar, N. Clark, I.M. Jiang, F.J. Kao, H. Liu, and H. Nohira, *Langmuir* **14**, 4330-4341 (1998).
- [P12] "SPONTANEOUS FORMATION OF MACROSCOPIC CHIRAL DOMAINS IN A FLUID SMECTIC PHASE OF ACHIRAL MOLECULES," D.R. Link, G. Natale, R.F. Shao, J.E. MacLennan, N.A. Clark, E. Korblova, and D.M. Walba, *Science* **278**, 1924-27 (1997).
- [P13] "QUANTUM CHEMISTRY BASED FORCE FIELDS FOR SOFT MATTER", M.A. Glaser, N.A. Clark, E. Garcia, and D.M. Walba, *Spectrochimica Acta A* **53**, 1325-1340 (1997). [selected by the *Spectrochimica Acta* editors as one of the 10 best papers published in *Spectrochimica Acta* in 1997].

- [P14] "SCALING MODEL OF ANNIHILATION-DIFFUSION KINETICS FOR CHARGED PARTICLES WITH LONG-RANGE INTERACTION," S.F. Burlatsky, V.V. Ginzburg, and N.A. Clark, *Physical Review E* **54**, R1056-R1057 (1996).
- [P15] "SIMULTANEOUS OBSERVATION OF LONGITUDINAL AND TRANSVERSE FERRO-ELECTRICITY IN FREELY SUSPENDED FILMS OF AN ANTIFERROELECTRIC LIQUID CRYSTAL," D. Link, J.E. MacLennan, and N.A. Clark, *Physical Review Letters*, **41** 81 (1996).

Presentations

- [C1] "DOUBLE WELL INTERLAYER INTERACTION POTENTIALS IN TILTED SMECTICS," D. Link, G. Natale, J.E. MacLennan, and N.A. Clark, *Bulletin of the American Physical Society* **43**, 864 (1998).
- [C2] "ELECTRIC FIELD INDUCED RING PATTERNS IN FREELY SUSPENDED LIQUID CRYSTAL FILMS," G. Natale, D. Link, J.E. MacLennan, L. Radzihovsky, and N.A. Clark, *Bulletin of the American Physical Society* **43**, 729 (1998).
- [C3] "MICROSCOPIC ORGANIZATION OF THE SMECTIC C PHASE," M.A. Glaser, Y. Lansac, T. Weider, and N.A. Clark, *Bulletin of the American Physical Society* **43**, 864 (1998).
- [C4] "SPONTANEOUS FORMATION OF A CHIRAL FLUID PHASE FROM ACHIRAL MOLECULES," N.A. Clark, D.R. Link, G. Natale, R.F. Shao, J.E. MacLennan, E. Körblova, and D.M. Walba, presented at the 17th International Liquid Crystal Conference, July, 1998.
- [C5] "EVIDENCE FOR A DOUBLE WELL INTERLAYER INTERACTION POTENTIAL IN THE SMECTIC C PHASE," D. Link, G. Natale, J.E. MacLennan, and N.A. Clark, presented at the 17th International Liquid Crystal Conference, July, 1998.
- [C6] "ANTICLINIC TILTED SURFACES ON FREELY SUSPENDED SMECTIC C FILMS," D. Link, G. Natale, J.E. MacLennan, N.A. Clark, M. Walsh, S.S. Keast, and M.E. Neubert, presented at the 17th International Liquid Crystal Conference, July, 1998.
- [C7] "FREELY SUSPENDED FILMS OF BANANA SHAPED MESOGENS," D. Link, G. Natale, J.E. MacLennan, and N.A. Clark, presented at the 17th International Liquid Crystal Conference, July, 1998.
- [C8] "NANOSEGREATION OF POLYMER PRECURSORS IN SMECTIC HOSTS," M.A. Glaser, Y. Lansac, and N.A. Clark, *Bulletin of the American Physical Society* **42**, 199 (1997).
- [C9] "PAIR ANNIHILATION OF TOPOLOGICAL DEFECTS IN FREELY SUSPENDED FILMS OF A SMECTIC C LIQUID CRYSTAL MATERIAL," D.R. Link, A. Tewary, V.V. Ginzburg and N.A. Clark, *Bulletin of the American Physical Society* **42**, 308 (1997).
- [C10] "KINETICS OF A TWO-SPECIES ANNIHILATION WITH LONG RANGE INTERACTIONS," V. Ginzburg, L. Radzihovsky, and N.A. Clark, *Bulletin of the American Physical Society* **42**, 366 (1997).
- [C11] "COMPRESSION INDUCED SMECTIC C TO SMECTIC A TRANSITIONS IN A FREELY SUSPENDED LIQUID CRYSTAL FILM," D.R. Link, A. Tewary, and N.A. Clark, *Bulletin of the American Physical Society* **42**, 382 (1997).
- [C12] "LONGITUDINAL AND TRANSVERSE FERRO-ELECTRICITY IN FREELY SUSPENDED FILMS OF AN ANTIFERROELECTRIC LIQUID CRYSTAL," D.R. Link, J.E. MacLennan, and N.A. Clark, Sixth International Conference on Ferroelectric Liquid Crystals, Brest, France (1997).
- [C13] "NANOSEGREATION OF POLYMER PRECURSORS IN SMECTIC HOSTS," M.A. Glaser, Y. Lansac, and N.A. Clark, Sixth International Conference on Ferroelectric Liquid Crystals, Brest, France (1997).
- [C14] "ELECTRIC FIELD-INDUCED RING PATTERNS IN FREELY SUSPENDED FERROELECTRIC LIQUID CRYSTAL FILMS," D.R. Link, J.E. MacLennan, L. Radzihovsky, and N.A. Clark, Sixth International Conference on Ferroelectric Liquid Crystals, Brest, France (1997).

- [C15] "ATOMISTIC SIMULATION OF PHOTO-INDUCED INSTABILITIES IN SMECTIC A LIQUID CRYSTALS," Y. Lansac, M.A. Glaser, and N.A. Clark, 1997 American Physical Society Meeting on Computational Physics.

Invited conference presentations

- [I1] "THE SMECTIC XP PHASES: CHIRAL LIQUID CRYSTALS FROM ACHIRAL MOLECULES," Fifth International Display Workshops of the Society for Information Display, Kobe, Japan (1998).
- [I2] "SPONTANEOUS FORMATION OF CHIRAL FLUID PHASES FROM ACHIRAL MOLECULES," Fourth NASA Microgravity Fluid Physics and Transport Phenomena Conference, Cleveland, OH (1998).
- [I3] "RECENT RESULTS ON SPONTANEOUSLY CHIRAL PHASES OF BENT-CORE MOLECULES," ALCOM Workshop on Banana-Shaped Liquid Crystal Molecules, Kent, OH (1998).
- [I4] "CHIRALITY AND FERROELECTRICITY IN LIQUID CRYSTALS," Sixth International Conference on Ferroelectric Liquid Crystals, Brest, France (1997).
- [I5] "SOME OBSERVATIONS REGARDING ACHIRAL POLAR SMECTIC PHASES," Sixth International Conference on Ferroelectric Liquid Crystals, Brest, France (1997).
- [I6] "FERROELECTRIC LIQUID CRYSTAL DISPLAYS," Seventeenth International Display Research Conference Toronto, Canada (1997).
- [I7] "SPONTANEOUS FORMATION OF POLAR CHIRAL LAYERS FROM ACHIRAL MOLECULES IN A NOVEL ANTIFERROELECTRIC SMECTIC LIQUID CRYSTAL PHASE," Workshop on Banana-Shaped Liquid Crystals, Berlin, Germany (1997).
- [I8] "SIMULTANEOUS OBSERVATION OF ELECTRIC FIELD COUPLING TO LONGITUDINAL AND TRANSVERSE FERROELECTRICITY IN A CHIRAL LIQUID CRYSTAL," Workshop on Banana-Shaped Liquid Crystals, Berlin, Germany (1997).
- [I9] "STRUCTURE, HYDRODYNAMICS, AND PHASE TRANSITIONS OF FREELY SUSPENDED LIQUID CRYSTALS," Third NASA Microgravity Fluid Physics Conference, Cleveland, OH (1996).

Ph.D. theses

- [T1] "SYMMETRY AND STRUCTURE OF FREELY SUSPENDED FILMS," D.R. Link, University of Colorado, Department of Physics (1998).

REFERENCES CITED

- [1] P. S. Pershan, *Structure of Liquid Crystal Phases*, World, Singapore (1988).
- [2] C.Y. Young, R. Pindak, N.A. Clark and R.B. Meyer, *Phy. Rev. Lett.* **40**, 773 (1978).
- [3] C.Y. Young, R.B. Meyer and N.A. Clark, *Phys. Rev. Lett.* **45**, 1193 (1980).
- [4] C. Rosenblatt, R. Pindak, N.A. Clark and R.B. Meyer, *Phys. Rev. Lett.* **42**, 220 (1979)
- [5] D.H. Van Winkle and N.A. Clark, *Phys. Rev. Lett.* **53**, 1157 (1984).
- [6] D.J. Tweet, R. Hoyst, B.D. Swanson, H. Stragier, and L.B. Sorensen, *Phys. Rev. Lett.* **65**, 215 (1990).
- [7] Ch. Bahr and D. Fliegner, *Phys. Rev. Lett.* **70**, 1842 (1993).